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Publication date:
2012

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Citation (APA):

Mogensen, M. B. (Author). (2012). Production of 'Green Natural Gas' Using Solid Oxide Electrolysis Cells (SOEC): Status of Technology and Costs. Sound/Visual production (digital) <http://www.igu.org/wgc-2012>

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PRODUCTION OF 'GREEN NATURAL GAS' USING SOLID OXIDE ELECTROLYSIS CELLS (SOEC):

STATUS OF TECHNOLOGY AND COSTS

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Date: 05 June, 2012

Venue: EF5.A: WOC5 How To Integrate
Renewable Power In The NG grid



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Introduction

- **Wish to increase the production of sustainable and CO₂ neutral energy - "green house" effect – not enough inexpensive oil**
- **Denmark aims to become independent of fossil fuel by 2050.**

Energy strategy 2050 - from coal, oil and gas to green energy, The Danish Government, February 2011, http://www.ens.dk/Documents/Netboghandel%20-%20publikationer/2011/Energy_Strategy_2050.pdf

- **Natural to look for photosynthesis products (biomass), but not enough biomass**

H. Wenzel, "Breaking the biomass bottleneck of the fossil free society", Version 1, September 22nd, 2010, CONCITO, <http://www.concito.info/en/udgivelser.php>

Enough renewable energy?

- Fortunately, enough renewable energy is potentially available.
- The annual global influx from sun is ca. $3 - 4 \cdot 10^{24}$ J - marketed energy consumption is ca. $5 \cdot 10^{20}$ J;
 - 1) A. Evans et al., in: Proc. Photovoltaics 2010, H. Tanaka, K. Yamashita, Eds., p. 109.
 - 2) Earth's energy budget, Wikipedia, http://en.wikipedia.org/wiki/Earth's_energy_budget
 - 3) International Energy Outlook 2010, DOE/EIA-0484(2010), U.S. Energy Information Administration, <http://www.eia.gov/oiaf/ieo/index.html>
- Earth's surface receives at least ca. 6 - 8,000 times more energy than we need. In deserts, intensity is higher than average at the same latitude – dry air

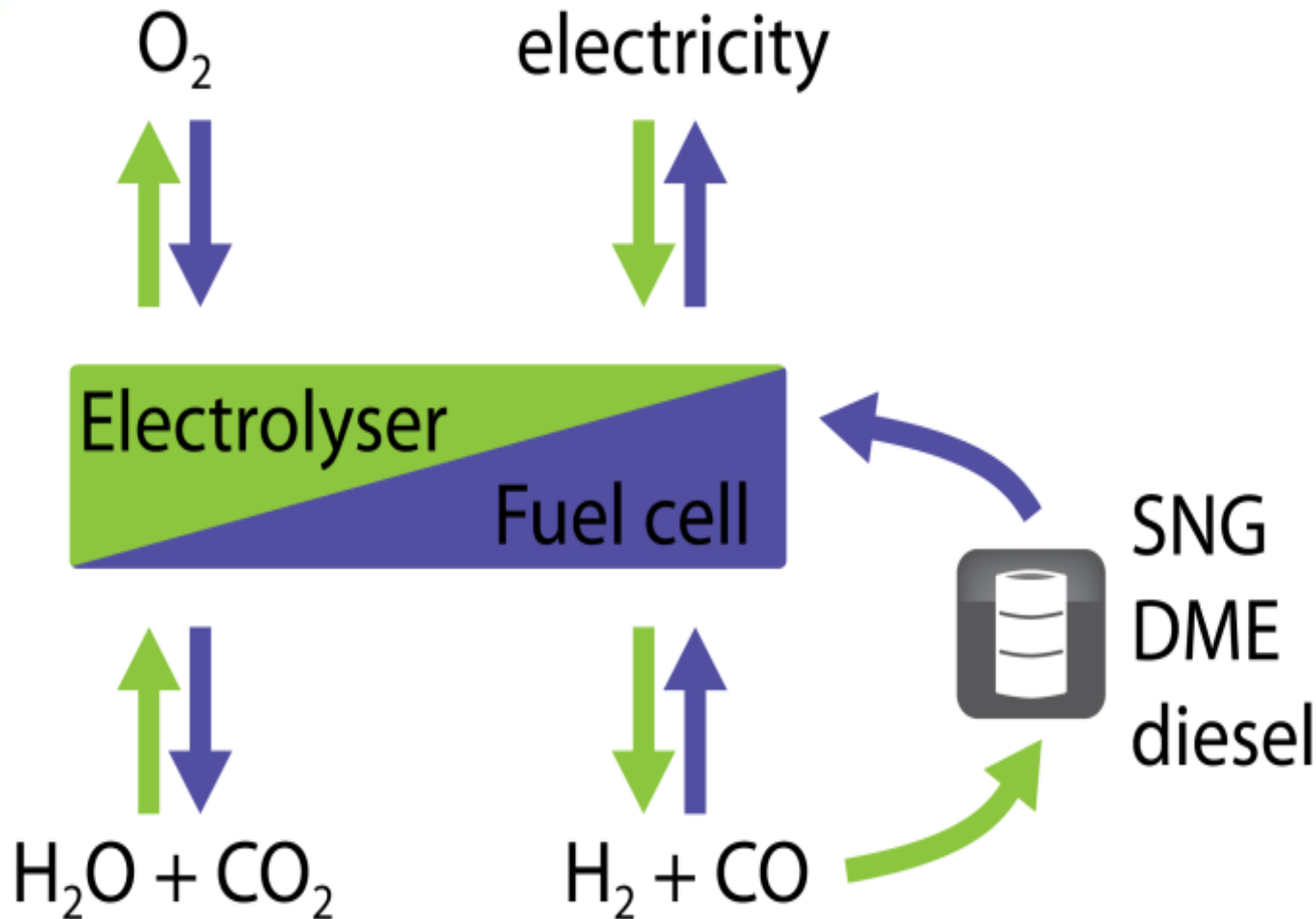
Area needed

- If 0.2 % of the earth's area (ca. 1 mill. km² or 15 % of Australia) and if collection efficiency = 10 %, we get enough energy.
- Besides solar we also have geothermal and nuclear (fusion and fission) potential energy sources.
- CO₂ free nuclear - more efficient if affordable storage technology is available.
- Important part of the solar energy is actually converted to biomass, hydro and wind energy – easier to harvest.

We need electrolysis

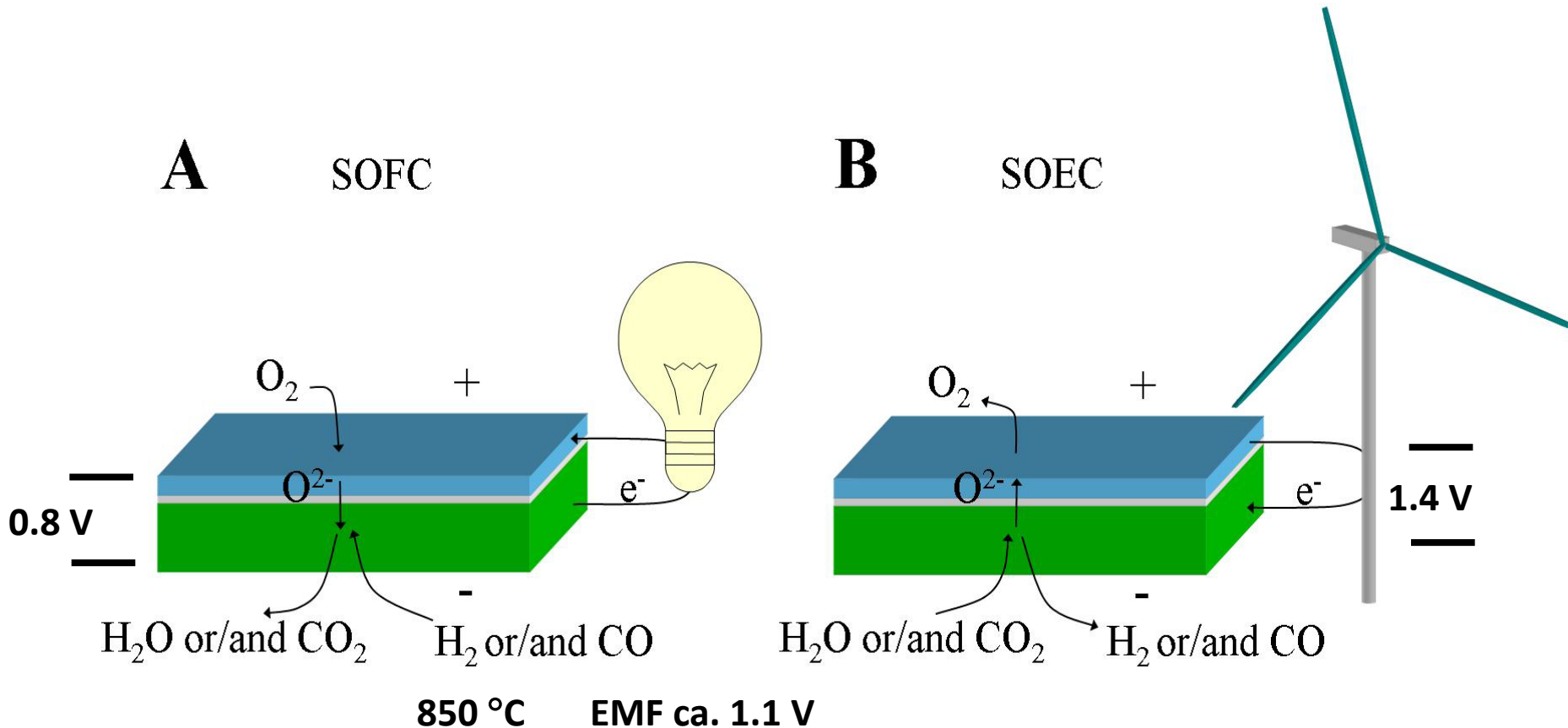
- Many technical principles are pointed out as suitable for storage technologies:
 - pumping of water to high altitudes
 - batteries
 - superconductor coil (magnetic storage)
 - flywheels
 - Thermo-chemical looping
 - Solar Thermal Electrochemical
 - Photo-electrochemical HER and CO₂ reduction
- Use electricity directly as much as possible!
- All very important! But: first 4 are not for long distance (> 500 km) transport sector. 3 last are early stage research - may prove efficient in the future.
- Therefore, within a foreseeable future: **Electrolysis is necessary in order to get enough renewable fuels!**

Reversible electrochemical cell



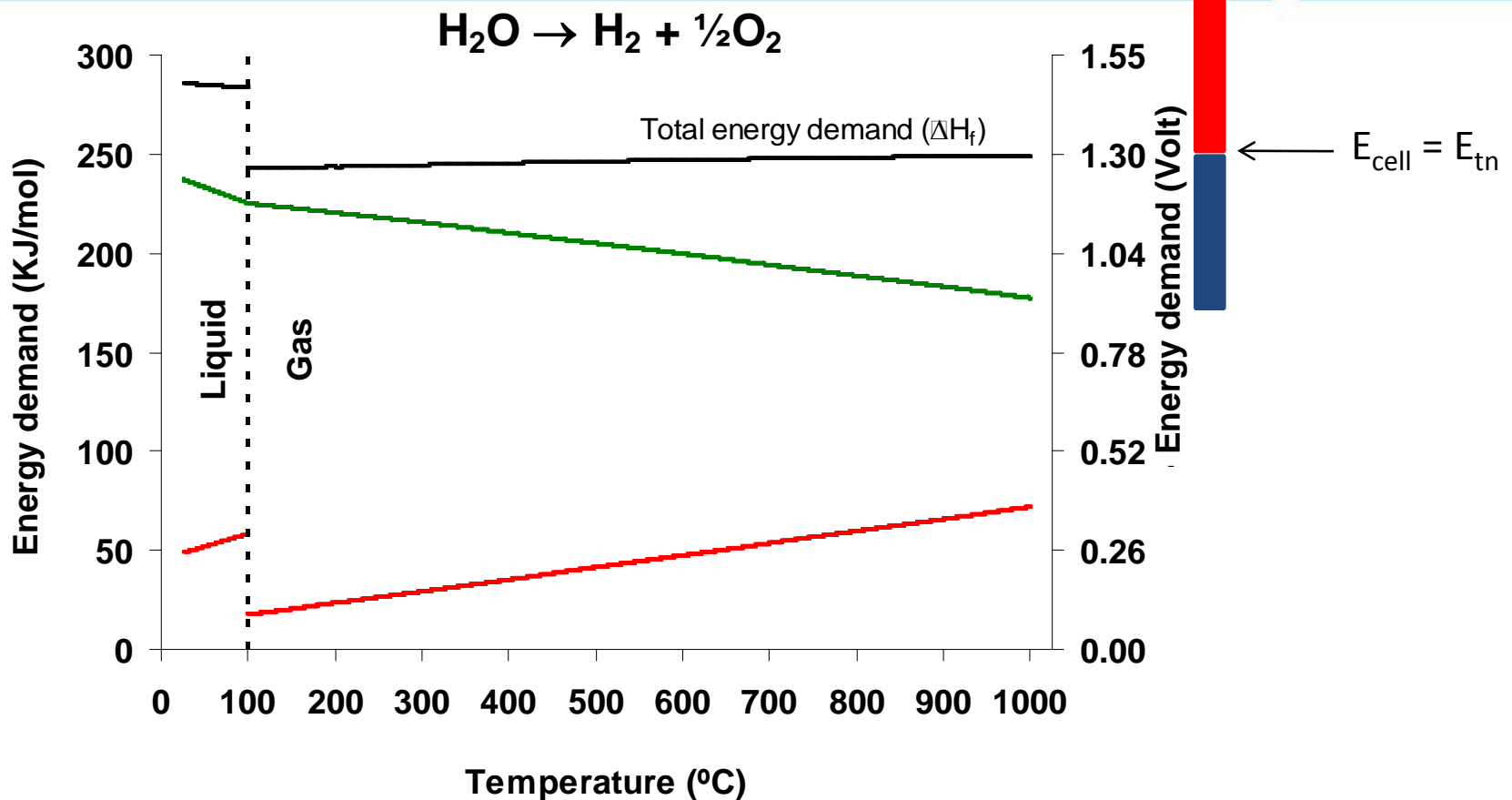
Reversible electrochemical cell - electrolyser for production of GNG, i.e. methane (SNG) and dimethyl ether (DME), or diesel – and fuel cell for electric power generation

Principle of fuel cell and electrolyser (SOC)



Working principle of a reversible Solid Oxide Cell (SOC). The cell can be operated as a fuel cell, SOFC (A), and as an electrolysis cell, SOEC (B).

Why SOC? Thermodynamics



Energy ("volt") = Energy (kJ/mol)/2F

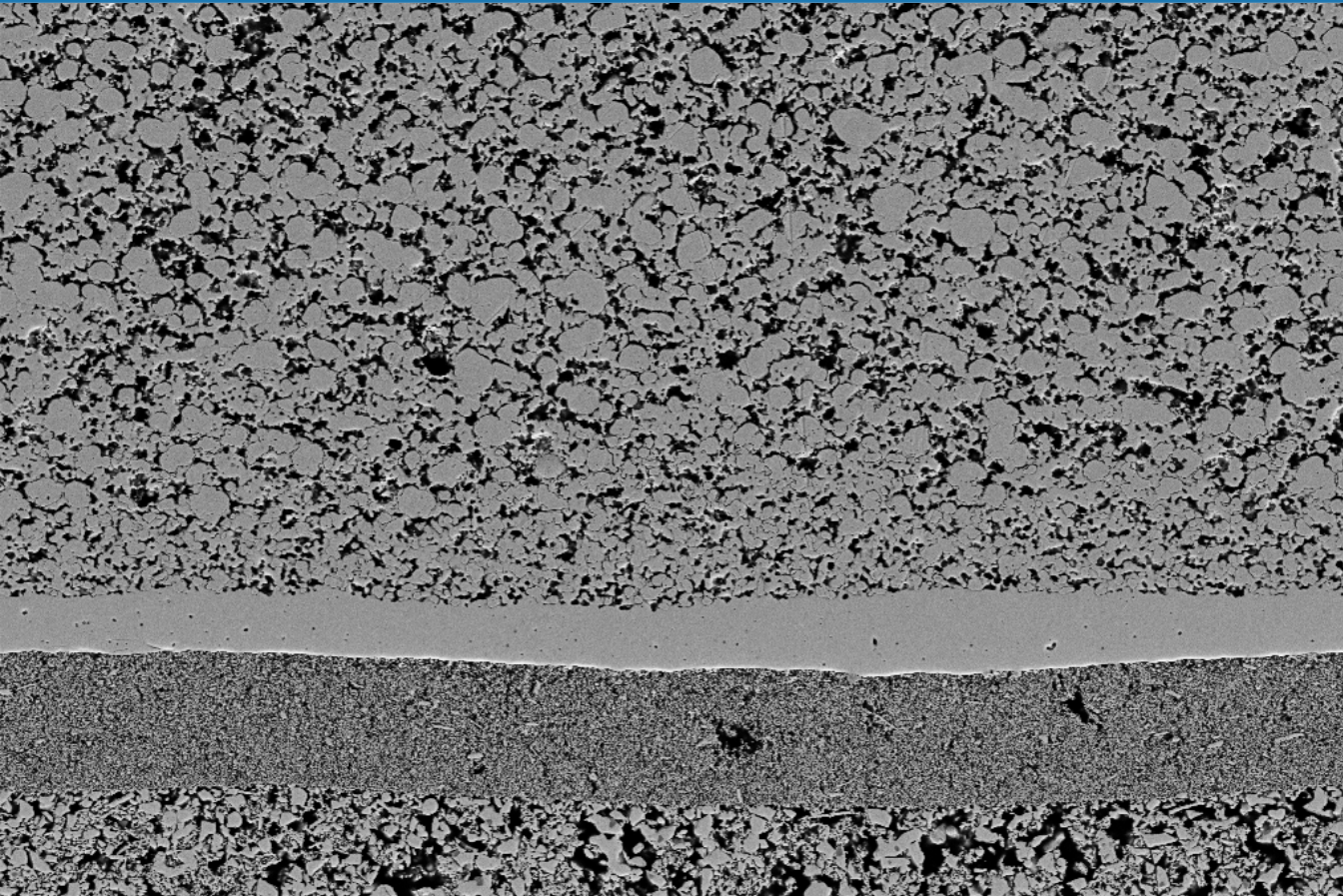
$E_{\text{tn}} = \Delta H/2F$ = Thermoneutral potential

$i \propto E_{\text{cell}} - \Delta G/2F$

Price $\propto 1/i$ [A/cm²],

$\Delta H/\Delta G > 1$, $\eta = 100\%$ at $E = E_{\text{tn}}$ (no heat loss)

Ni-YSZ supported SOC



Ni/YSZ support

Ni/YSZ electrode

YSZ electrolyte

LSM-YSZ electrode

10 μm Acc. voltage: 12 kV SE image

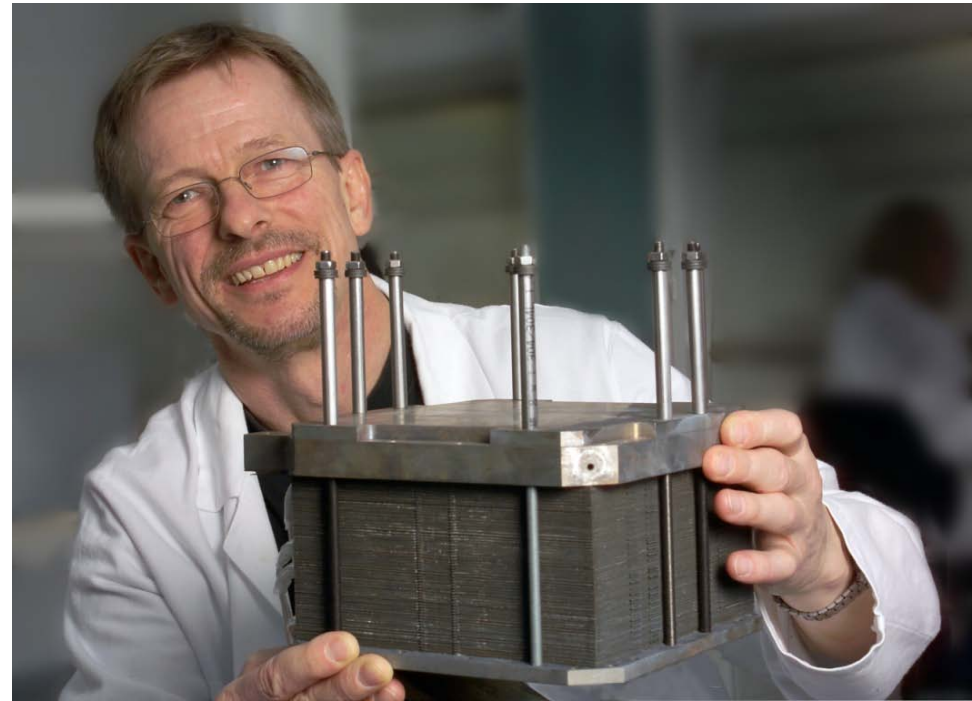
LSM = Lanthanum Strontium Manganate

YSZ = Yttria Stabilized Zirconia

Ni = Nickel

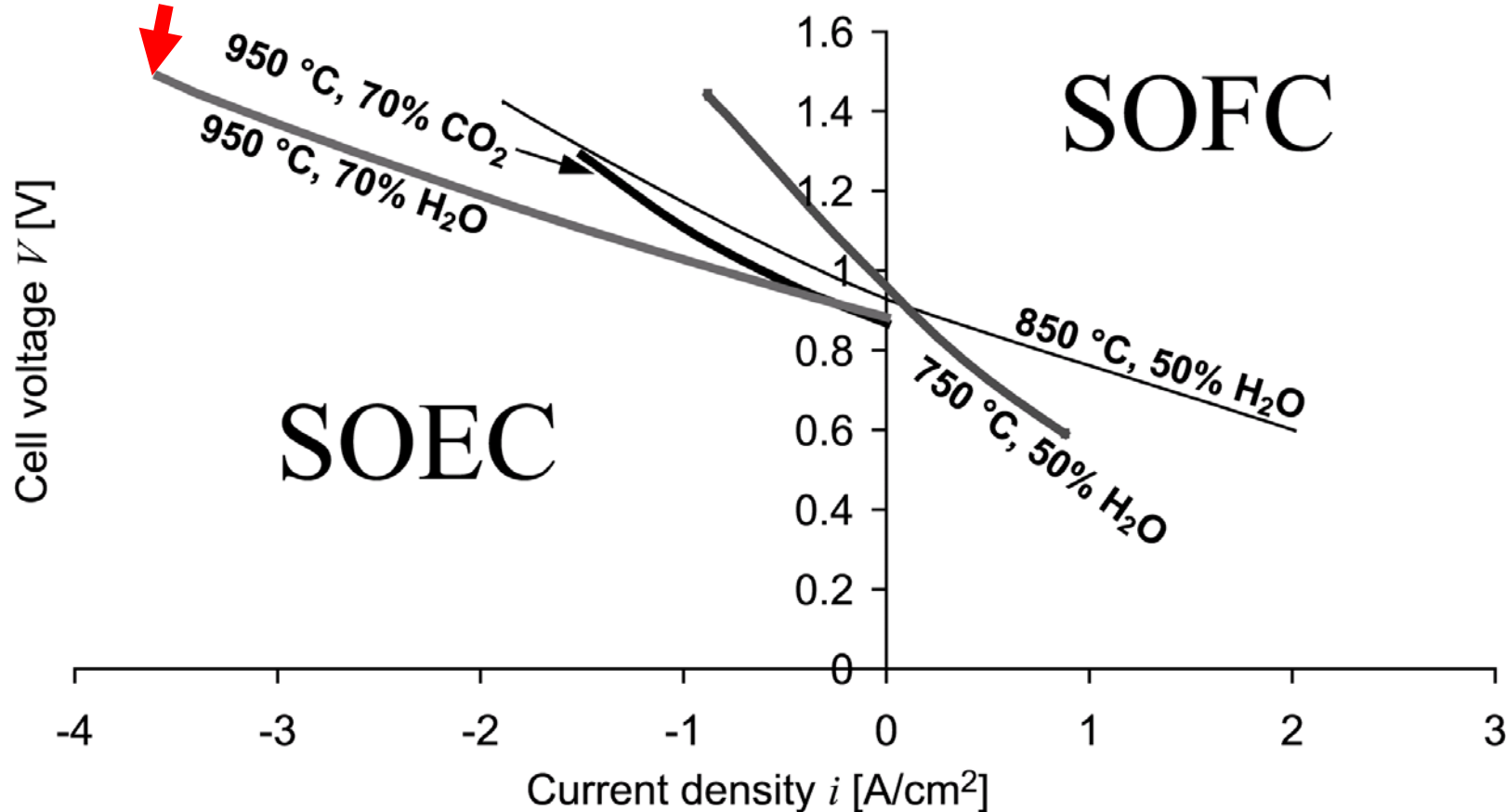
Cells stacks

- To operate at useful voltages several cells, e.g. 50, are stacked in series
- High energy density: Stack electric power density of ~ 3 kW/liter demonstrated with Topsoe cell stacks in electrolysis mode
- Scalable technology:
From kW to MW



Cell performance

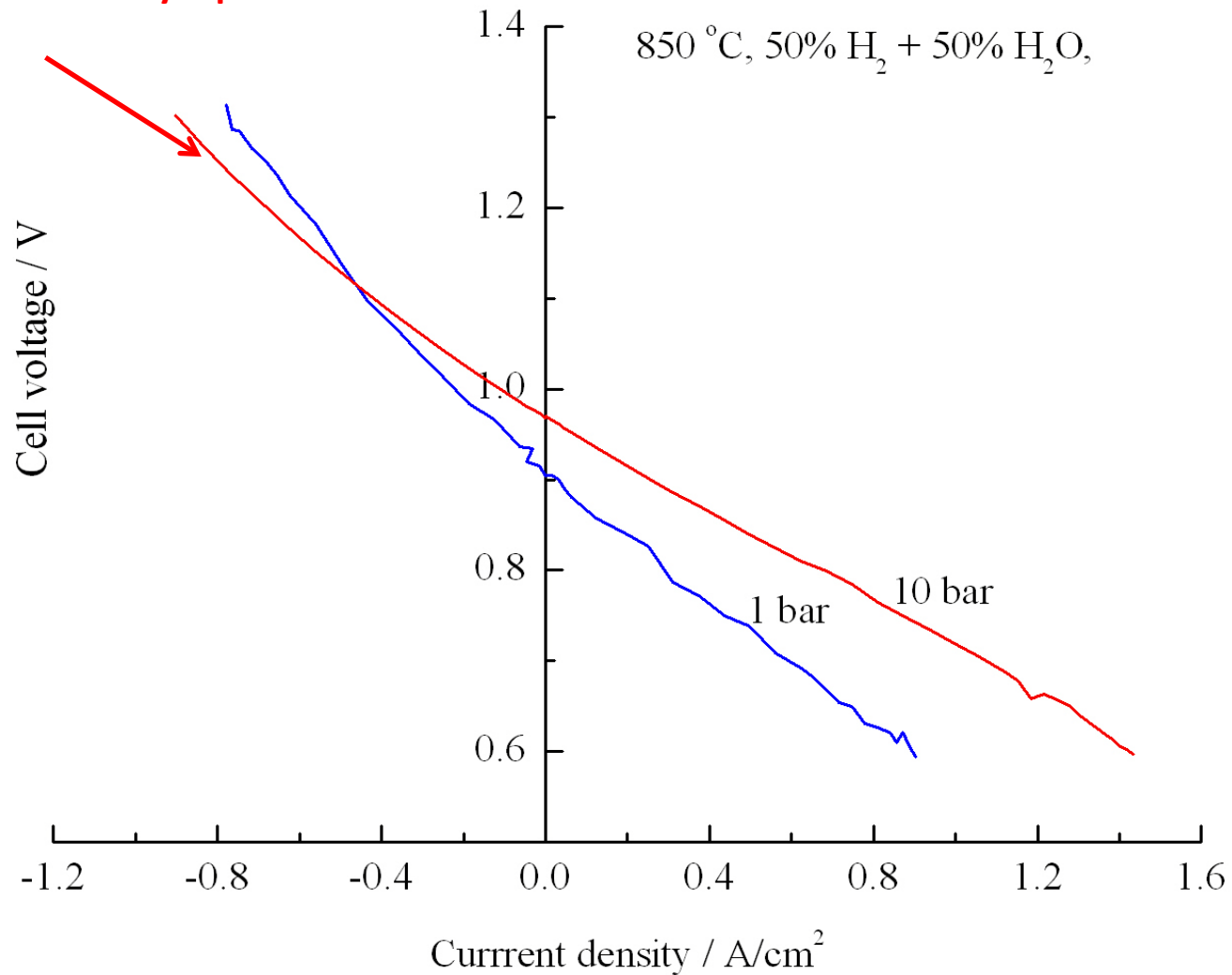
World record !



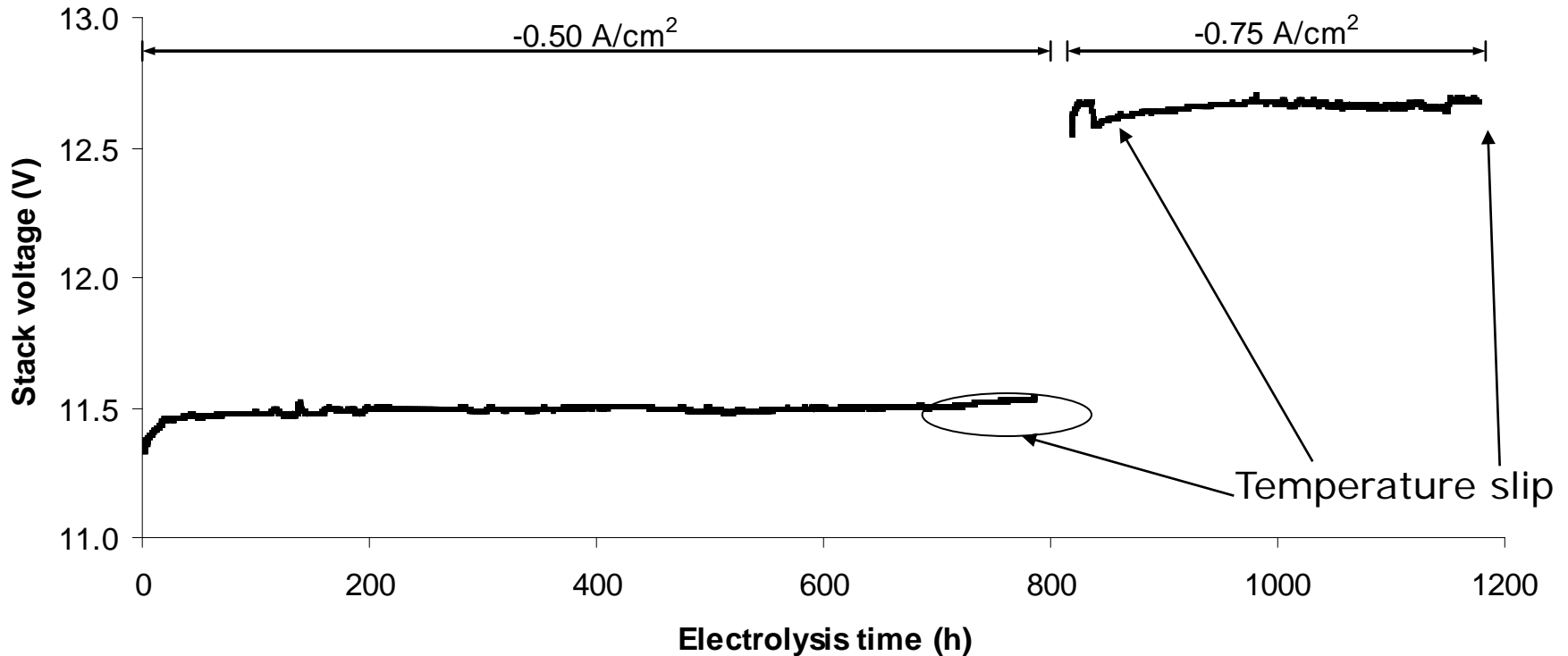
i - *V* curves for a Ni-YSZ-supported Ni/YSZ/LSM SOC: electrolyzer (negative cd) and fuel cell (positive cd) at different temperatures and steam or CO₂ partial pressures - balance is H₂ or CO. S.H. Jensen et al., International Journal of Hydrogen Energy, **32** (2007) 3253

Some early results

We get pressurized hydrogen with lower electricity input!



1 kW - 10-cell Topsoe stack – 12×12 cm², Risø DTU test



**850 °C, -0.50 A/cm² or -0.75 A/cm², 45 % CO² / 45% H₂O / 10 % H₂,
cleaned gases.**

S. Ebbesen et al., Int. J. Hydrogen Energy, **36**, (2011) 7363

Production of syngas (SOEC case)

Reaction Schemes:

The overall reaction for the electrolysis of steam plus CO₂ is:



This is composed of three partial reactions. At the negative electrode:



and at the positive electrode:



Methane, Methanol and DME synthesis

- $\text{CO} + 3 \text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$
- Ni - based catalysts
- 190 °C – 450 °C
- 3 MPa, i.e. pressurized
- in principle possible to produce inside SOEC stack on Ni-electrode - but very low equilibrium CH_4 concentration at 650 °C and above

- $\text{CO} + 2 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$
- $2 \text{CO} + 4 \text{H}_2 \rightleftharpoons (\text{CH}_3)_2\text{O} + \text{H}_2\text{O}$
- Cu/ZnO- Al_2O_3 catalyst
- 200 °C - 300 °C
- 4.5 - 6 MPa, again the electrolyser should be pressurized

- Another route to CO/syngas via shift reaction: $\text{H}_2 + \text{CO}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO}$

Why synthetic hydrocarbons?

The energy density argument

Comparison of Energy Storage Types. Only the batteries are including containers.

Storage type	MJ/L	MJ/kg	Boiling point, °C
Gasoline	33	46	40 – 200
Dimethyl ether - DME	22	30	- 25
Liquid methane	24	56	-162
Liquid hydrogen	10	141	-253
Compressed air – 20 MPa	0.1	0.4	
Water at 100 m elevation	10^{-3}	10^{-3}	
Lead acid batteries	0.4	0.15	
Li-ion batteries	1	0.5	

Why synthetic fuel? The power density argument

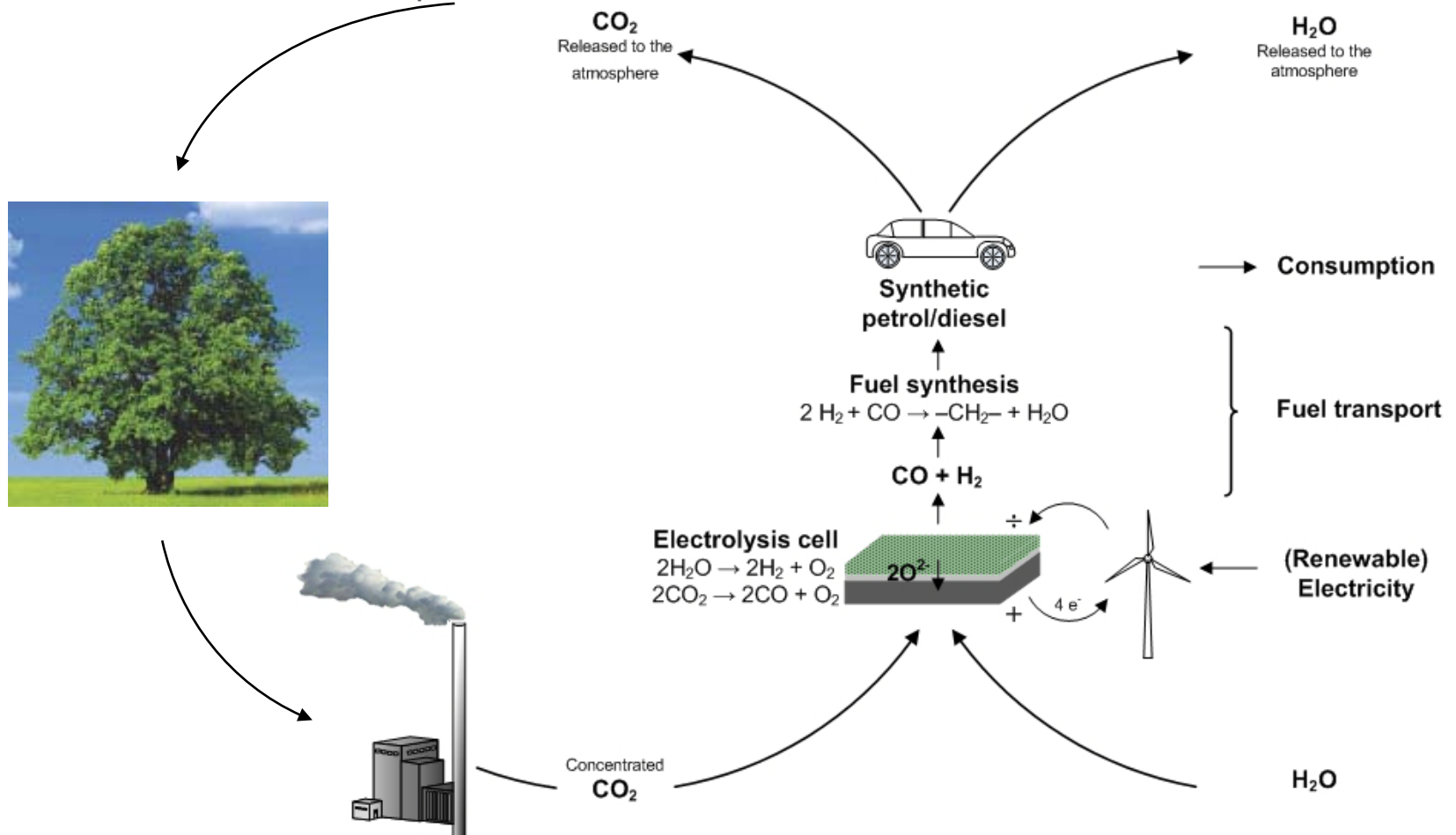
- Gasoline filling rate of 20 L/min equivalents 11 MW of power and means it takes 2½ min to get 50 l = 1650 MJ on board
- For comparison: Li-batteries usually requires 8 h to get recharged. For a 300 kg battery package (0.5 MJ/kg) this means a power of ca. 3.5 kW i.e. it takes 8 h to get 150 MJ on board.
- The ratio between their driving ranges is only ca. 5, because the battery-electric-engine has an efficiency of ca. 70 % - the gasoline engine has ca. 25 %.

Visions for synfuels from electrolysis of steam and carbon dioxide

- 1. Big off-shore wind turbine parks coupled to a large SOEC – produce CH_4 (synthetic natural gas, SNG) - feed into existing natural gas net-work (in Denmark).**
- 2. Large SOEC systems - produce DME, gasoline and diesel - Island, Canada, Greenland, Argentina, Australia ... geothermal, hydro, solar and wind.**
- 3. Target market: replacement of natural gas and liquid fuels for transportation**
- 4. All the infrastructure exists!!**

Vision, Biomass - CO₂ recycling

Short term realisation - CO₂ capture from industrial sources



New SOC production facility

Topsoe Fuel Cell A/S

DTU Energy Conversion, Haldor Topsoe A/S and Topsoe Fuel Cell A/S have close cooperation around solid oxide cell technology.

- Inauguration: April 2009
- Capacity \approx 5 MW/yr
- Investment: >13 mio. EUR



Advanced technology – industrial relevance – low production cost



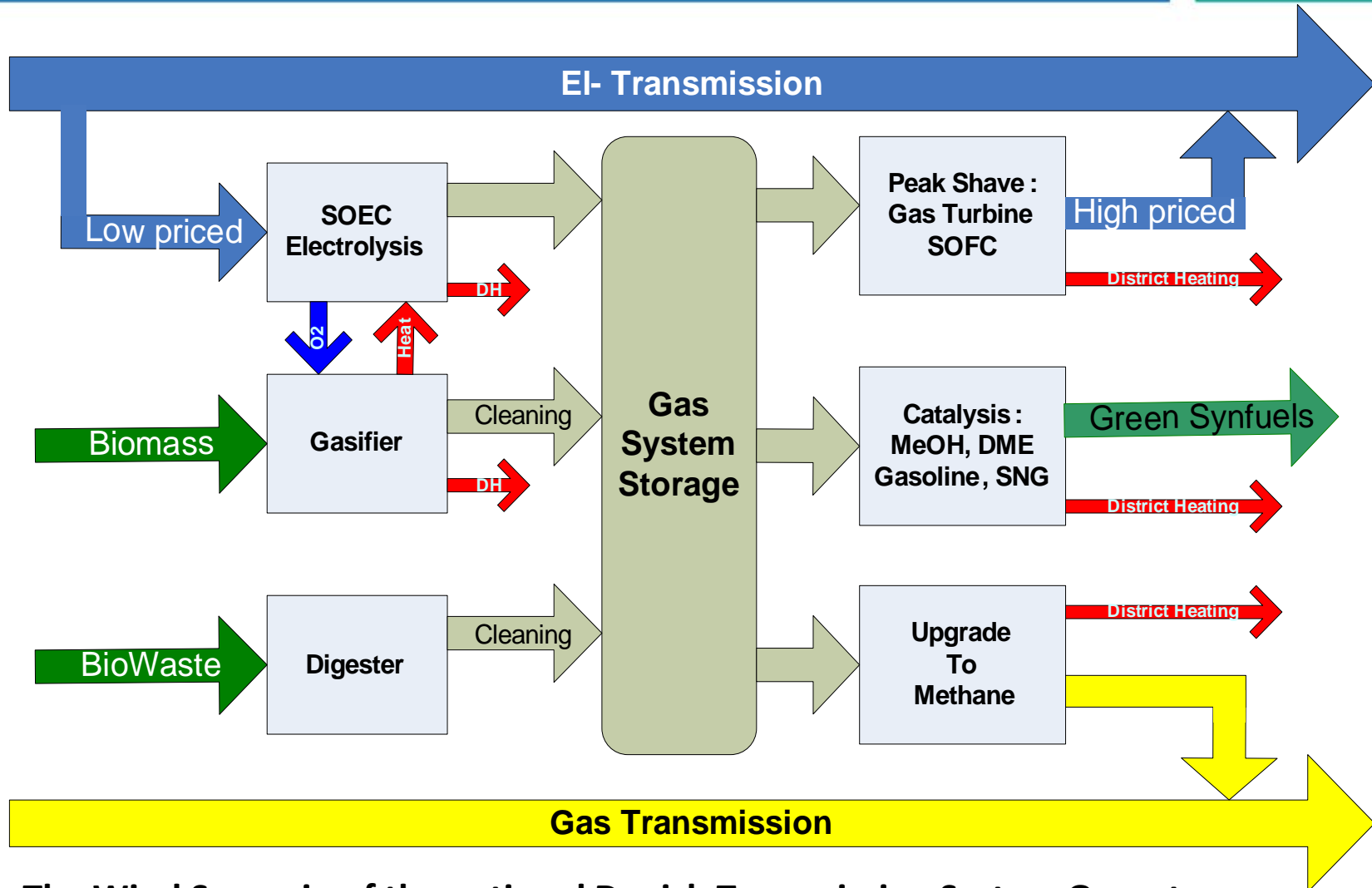
Topsoe SynGas Technologies



- Synthesis Gas
- Ammonia
- Hydrogen
- Carbon Monoxide
- SNG
- Methanol
- DME
- Gasoline - TIGAS

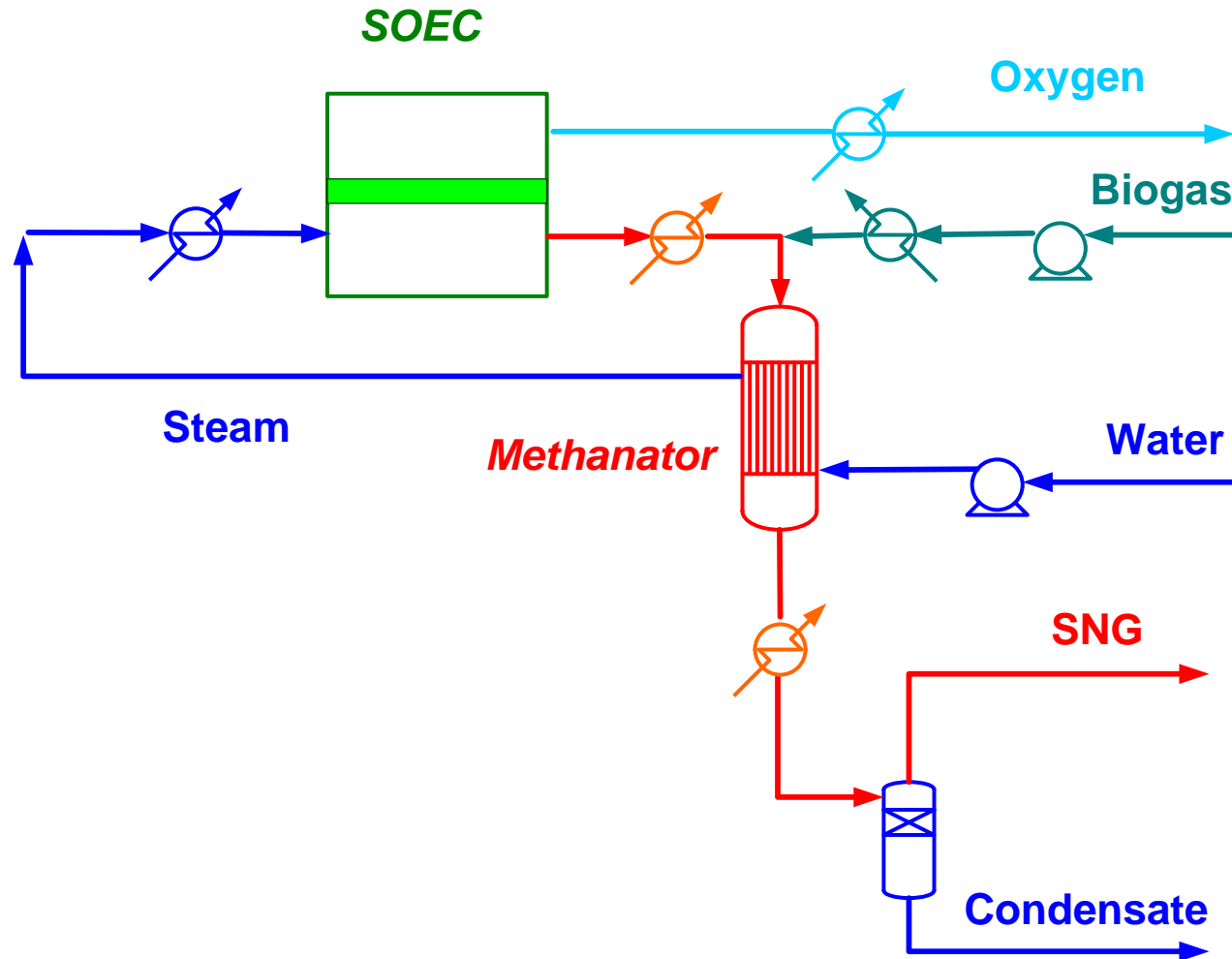


Combining Technologies

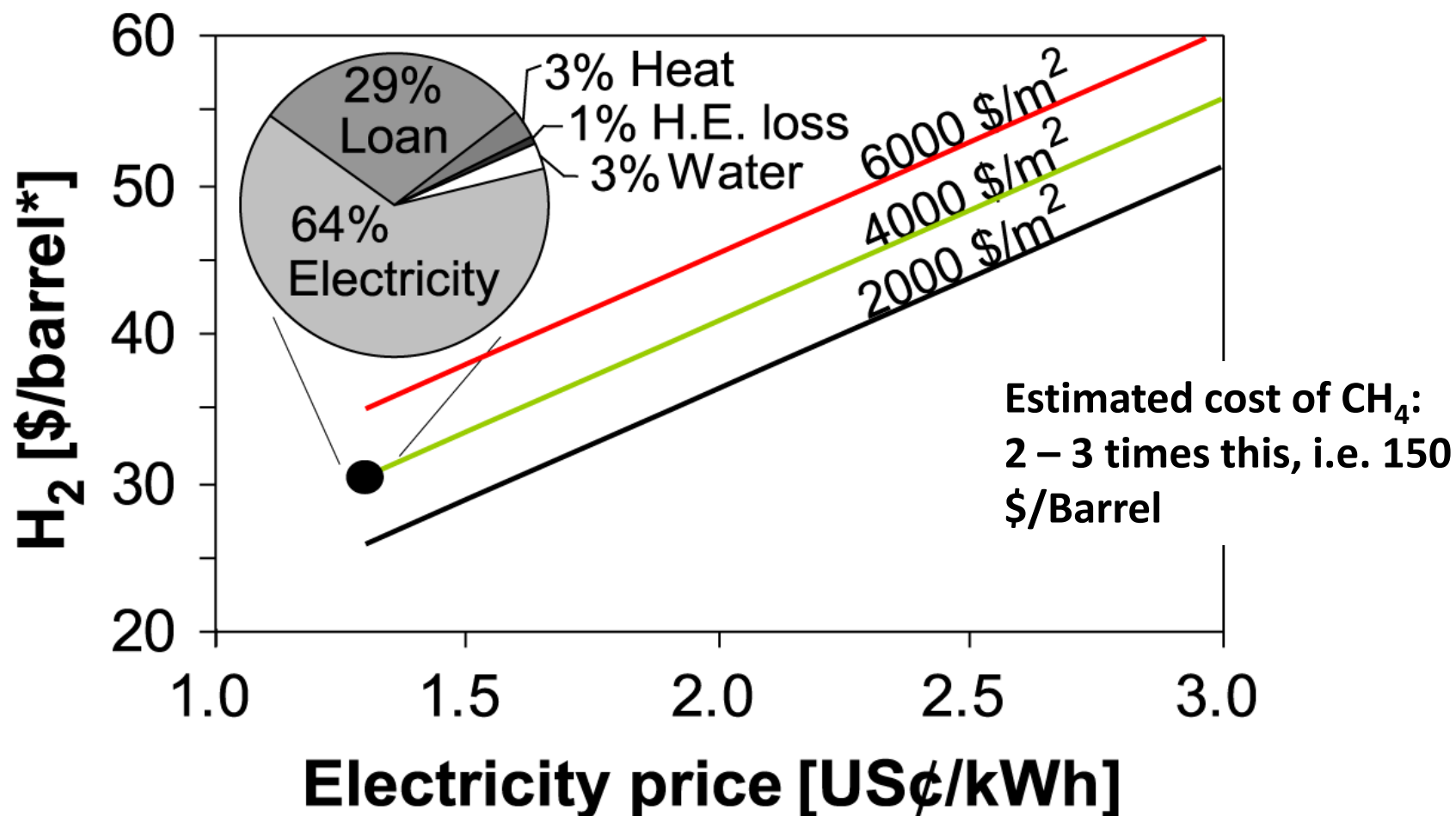


The Wind Scenario of the national Danish Transmission System Operator, Energinet.dk's visions for a fossil fuel free Denmark in 2050

Biogas to SNG via SOEC and methanation of the CO_2 in the biogas



H₂ production – economy estimation



* Conversion of H₂ to equivalent crude oil price is on a pure energy content (J/kg) basis




Problems in commercialization

- **Costs, costs and costs, which have different disguises:**
 - **Fabrication cost**
 - **Performance/efficiency**
 - **Durability**
- **Risk = reliability**
- **Annoyance and disturbance of people (noise, vibration, ugly appearance,.....)**

We have to improve it all – and it is a never ending process

Acknowledgement

I acknowledge support from our sponsors

- Danish Energy Authority  DANISH ENERGY AUTHORITY
- Energinet.dk 
- EU 
- Topsoe Fuel Cell A/S 
clean, efficient and reliable
- Danish Programme Committee for Energy and Environment
- Danish Programme Committee for Nano Science and Technology, Biotechnology and IT
- The work of many colleagues over the years